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PHOTOGRAPHIC EMULSION

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7 Claims. (Cl. 95—7)

Our present invention relates to a photographic emulsion and more particularly to a light sensitive emulsion layer capable of yielding a direct positive.

It is known to incorporate sensitizers into photographic emulsions capable of yielding direct positives by exposure and development. By these sensitizers the sensitivity to light of the emulsions is greatly increased in the range of the long wave rays, but the intrinsic sensitivity thereof is often lowered in the range of short wave length. Moreover, it has been observed that in sensitizing an ordinary photographic emulsion the decrease of its intrinsic sensitivity is especially remarkable if the sensitizer is added in a greater amount than necessary for reaching a sufficient sensitizing effect. It is also known that sensitizers added in excess to ordinary emulsions are capable of absorbing the light to which they render the emulsions sensitive, i. e. they have the property of filter dyes.

Our present invention has as an object to provide a photographic emulsion directly yielding a positive image and possessing a high total sensitivity.

Further objects will be apparent from the following description.

These objects are accomplished by adding a great amount of a sensitizer to an emulsion suitable for the direct production of positives by exposure and development. By this addition the intrinsic sensitivity of the emulsion is not reduced but considerably increased. Moreover, even the total sensitivity of the emulsion is enhanced by this means which was not to be expected.

Such an emulsion ("direct positive" emulsion) may, for instance, be prepared by incorporating into a silver halide emulsion a substance which causes fog and then heating the emulsion in the manner as described in U. S. P. No. 2,005,837. It may also be produced by a treatment with X-rays in the manner described in British Patent No. 443,245 or by a treatment with ultraviolet, visible or infra-red rays in the manner as described in German Patent No. 693,917.

All classes of the sensitizing dyestuffs include sensitizers especially useful for the improvement according to the invention. There are sensitizers which render the emulsion especially strongly sensitive, for instance to an extent that a sensitivity of 120 times the original sensitivity is attained. In this case, however, only a flat gradation curve is generally obtained. There are also sensitizers which do not increase the sensitivity in such an extent, but are capable of improving the gradation curve. Further sensitizers only slightly increase the sensitivity, but yield a very favourable reversal gradation curve. The choice of the sensitizers therefore depends upon their intended use.

The dyestuffs from the large number of the cyanines, isocyanines, pseudocyanines and symmetric or unsymmetric methinecyanines having three or more carbon atoms in the methine chain are suitable to increase the sensitivity of "direct positive" emulsions. The dyestuffs may contain simple or substituted nuclei of oxazole, quinoline, thiazole, indole, selenazole and imidazole, if desired condensed with benzene-, naphthalene- or other nuclei. Further suitable compounds are rhodacyanines, merocyanines, styryl compounds and phthalein dyestuffs.

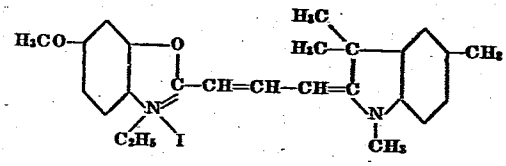
The quantities of the sensitizers to be used in the present invention amount to a multiple of the quantity normally added (about 20–40 mg. for 1 kilo of emulsion) especially to more than 100 mg. for 1 kilo of emulsion. The optimum quantity generally about 110–250 mg. for 1 kilo of emulsion must be tested in each case.

The following examples illustrate the invention, but they are not intended to limit it thereto. The "direct positive" emulsions used in the examples have been prepared in the manner described in U. S. P. No. 2,005,837. The non-sensitized "direct positive" emulsion has the sensitivity of 1 (2°). By adding a normal amount of sensitizer the sensitivity of the "direct positive" emulsion is raised to 2^2–2^3, i. e. the sensitivity is increased fourfold to eightfold.

Orthochromatic Sensitizers

Example 1

To 1 kilo of a "direct positive" emulsion 150 mgrs. of a dyestuff corresponding with the following formula are added:



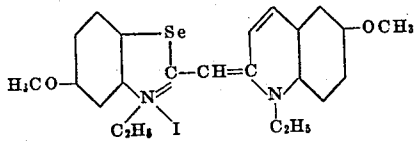
The dyestuff has been prepared in the manner as described in U. S. P. No. 2,080,551.

Increase of sensitivity: 2^4.

Example 2

To 1 kilo of a "direct positive" emulsion 150

mgrs. of a dyestuff corresponding with the following formula are added:

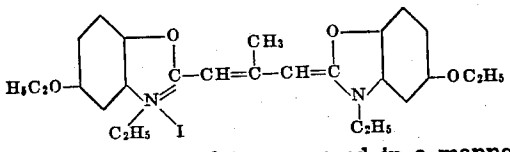


The dyestuff has been prepared in the manner as described in U. S. P. No. 2,052,754.

Increase of sensitivity: 2^4.

Example 3

To one kilo of a "direct positive" emulsion 150 mgrs. of a dyestuff of the following constitution are added:

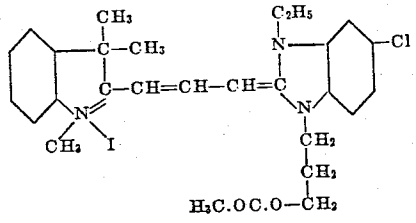


The dyestuff has been prepared in a manner analogous to that described in French Patent No. 765,724.

Increase of sensitivity: 2^4.

Example 4

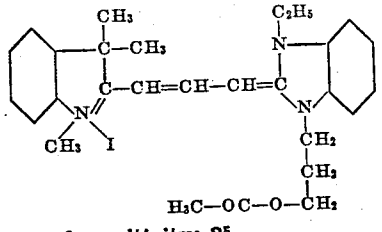
To one kilo of a "direct positive" emulsion 125 mgrs. of a dyestuff of the following constitution are added:



Increase of sensitivity: 2^6.

Example 5

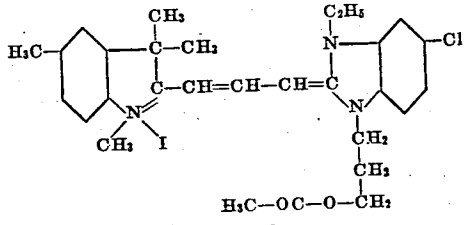
To one kilo of a "direct positive" emulsion 125 mgrs. of a dyestuff of the following constitution are added:



Increase of sensitivity: 2^5.

Example 6

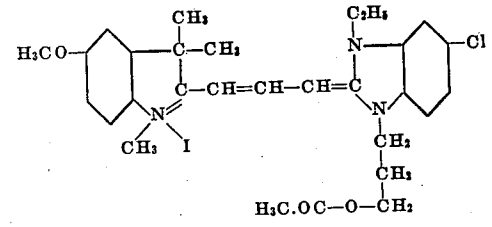
To 1 kilo of a "direct positive" emulsion 125 mgrs. of a dyestuff corresponding to the following formula are added:



Increase of sensitivity: 2^8.

Example 7

To 1 kilo of a "direct positive" emulsion 125 mgrs. of a dyestuff according to the following formula are added:

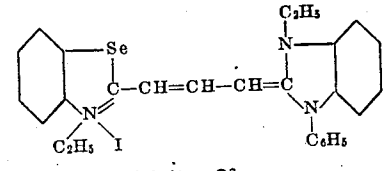


Increase of sensitivity: 2^7.

The dyestuffs disclosed in Examples 4 to 7 were prepared in the manner as described in Belgian Patent No. 436,660.

Example 8

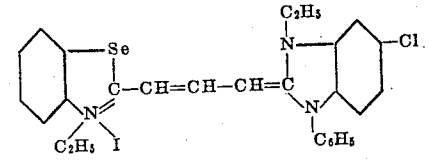
To 1 kilo of a "direct positive" emulsion 125 mgrs. of a dyestuff of the following constitution are added:



Increase of sensitivity: 2^6.

Example 9

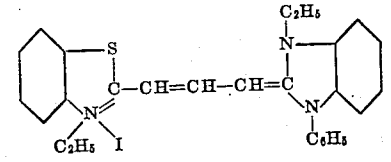
To 1 kilo of a "direct positive" emulsion 125 mgrs. of a dyestuff of the following constitution are added:



Increase of sensitivity: 2^7.

Example 10

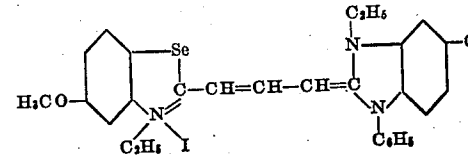
To 1 kilo of a "direct positive" emulsion 125 mgrs. of a dyestuff corresponding to the following formula are added:



Increase of sensitivity: 2^7.

Example 11

To 1 kilo of a "direct positive" emulsion 125 mgrs. of a dyestuff corresponding to the following formula are added:



Increase of sensitivity: above 2^7.

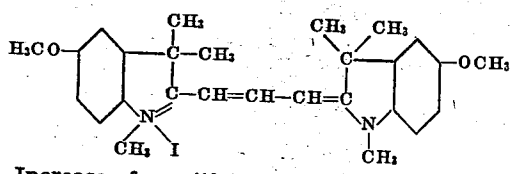
The dyestuffs defined in Examples 8 to 11 were produced in a manner analogous to that disclosed in French Patent No. 844,878.

PANCHROMATIC SENSITIZERS

Example 12

To 1 kilo of a "direct positive" emulsion 150

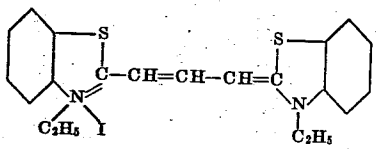
mgrs. of a dyestuff of the following constitution are added:



Increase of sensitivity: 2^4.

Example 13

To 1 kilo of a "direct positive" emulsion 120 mgrs. of a dyestuff of the following constitution are added:

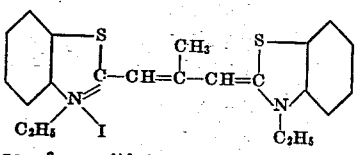


Increase of sensitivity: 2^5.

The dyestuffs described in Examples 12 and 13 were prepared corresponding to the manner disclosed in German Patent No. 410,487.

Example 14

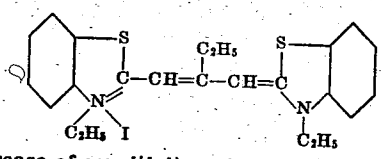
To 1 kilo of a "direct positive" emulsion 120 mgrs. of a dyestuff of the following constitution are added:



Increase of sensitivity: 2^6.

Example 15

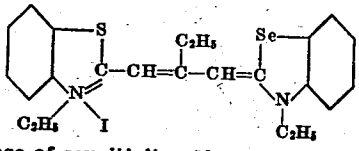
To one kilo of a "direct positive" emulsion 120 mgrs. of a dyestuff corresponding to the following formula are added:



Increase of sensitivity: 2^6.

Example 16

To 1 kilo of a "direct positive" emulsion 120 mgrs. of a dyestuff corresponding to the following formula are added:



Increase of sensitivity: 2^6.

The dyestuffs defined in Examples 14 to 16 were prepared in the manner disclosed in U. S. P. No. 2,107,379.

We claim:

1. A photographic silver halide emulsion fogged to such an extent that it is capable of directly yielding positive images by exposure and development and containing at least one sensitizing dyestuff, the quantity of said dyestuff being a multiple of the quantity normally used in sensitizing an emulsion but not greater than approximately 250 mg. to 1 kilo of emulsion, said fogging having taken place prior to the addition of said sensitizing dye.

2. A photographic silver halide emulsion fogged to such an extent that it is capable of directly yielding positive images by exposure and development and containing at least one sensitizing dyestuff in an amount ranging from about 100 to 250 mg. per kilo of emulsion, said fogging having taken place prior to the addition of said sensitizing dye.

3. A photographic material comprising a silver halide emulsion fogged to such an extent that it is capable of directly yielding positive images by exposure and development and containing at least one sensitizing dyestuff, the quantity of said dyestuff being a multiple of the quantity normally used in sensitizing an emulsion but not greater than approximately 250 mg. to 1 kilo of emulsion, said fogging having taken place prior to the addition of said sensitizing dye.

4. A photographic material comprising a silver halide emulsion fogged to such an extent that it is capable of yielding positive images by exposure and development and containing at least one sensitizing dyestuff in an amount ranging from about 100 to 250 mg. per kilo of emulsion, said fogging having taken place prior to the addition of said sensitizing dye.

5. A photographic silver halide emulsion fogged to such an extent that it is capable of directly yielding positive images by exposure and development and containing a trimethinecyanine sensitizer with an imidazole nucleus in an amount ranging from about 100 to 250 mg. per kilo of emulsion, said fogging having taken place prior to the addition of said sensitizing dye.

6. The article as defined in claim 4 wherein the sensitizing dyestuff is orthochromatic.

7. The article as defined in claim 4 wherein the sensitizing dyestuff is panchromatic.

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